Supporting Information

1. Preparation of cobalt supported onto silica

1.1. Reaction of 3-[3-(trimethylsilyl)propyl]-2,4-pentanedione with silica
Silica (Cab-O-Sil EH5 (4.5 SiOH/nm²; 380m²/g); 10g) was dried in vacuo at 100°C for 24 h. Dried toluene (240 ml) was then added under argon, followed by the addition of 3-[3-(trimethylsilyl)propyl]-2,4-pentanedione (MS-acac-H; 3.8 ml) under stirring. The mixture was heated at 105°C for 20h. After reaction, silica was recovered by centrifugation, followed by purification by repeated dispersion in toluene and centrifugation. The modified silica (Silica-MS-acac) was dried in vacuo at 80°C for 24h and stored under argon at room temperature.

1.2. Immobilization of cobalt onto silica
Modified silica (Silica-MS-acac; 7g) and Co(acac)₂ (2.08 g; 8 10⁻³ mol) were reacted under argon in a 500 ml flask containing dried toluene (250 ml). The mixture was stirred at room temperature for 72h. Cobalt supported onto silica was recovered by centrifugation, followed by repeated dispersions in toluene and centrifugations until the supernatant was colorless. The cobalt supported onto silica (Silica-Co(acac)) was dried in vacuo at 80°C for 24h and stored under argon at room temperature.

1.3. Infrared spectra of Cab-O-Sil, Silica-MS-acac, Silica-Co(acac) and Co(acac)₂

2. Preparation of cobalt supported onto the Merrifield resin

2.1. Grafting of acetylacetonate onto the Merrifield resin
Non porous Merrifield resin (2 mmol/g Cl; 70-150 mesh; 10g), sodium acetylacetonate (7.32 g; 6 10⁻³ mol) and NaI (0.3g; 2 10⁻³ mol) were added into a 250 ml flask and degassed by
three vacuum/argon cycles. Dried acetone (100 ml) was added and the mixture was stirred at room temperature overnight, followed by reaction at reflux for 5 days. The modified resin was filtered, washed with water and acetone before being dried in vacuo at 50°C for 24 h. The modified resin (Merrifield-(acac)) was stored under argon at room temperature.

2.2. Immobilization of cobalt onto the Merrifield resin
Modified Merrifield (Merrifield-Co(acac); 7.9 g) and Co(acac)$_2$ (13.9 g; 5.4 $10^{-4}$ mol) were added to a 250 ml flask and degassed by three vacuum/argon cycles. Dried toluene (150 ml) was added under argon and the mixture was stirred at room temperature for 2 days. The cobalt supported onto the Merrifield resin was recovered by centrifugation, followed by repeated dispersion in toluene and centrifugation until the supernatant was colorless. The cobalt supported onto the Merrifield resin (Merrifield-Co(acac)) was dried in vacuo at 80°C for 24h and stored under argon at room temperature.

2.3. Infrared spectra of the Merrifield, Merrifield-acac, Merrifield-Co(acac) and Co(acac)$_2$
3. Polymerization of VAc by the cobalt supported onto the Merrifield resin and recycling of the support

Cobalt supported onto Merrifield (Merrifield-Co(acac); 4g) and V70 (1.1757 g; 3.8 \times 10^{-3} \text{ mol}) were degassed by three vacuum/argon cycles. Degassed vinyl acetate (59 ml; 0.64 mol) was added, and the reaction medium was stirred at 30°C for 17h. A degassed solution of TEMPO (0.9925 g TEMPO (6.3 \times 10^{-3} \text{ mol}) in 59 ml of toluene) was then added to the reaction medium and the mixture was stirred at 30°C for 24h. The support was recovered by centrifugation and purified by repeated dispersion in toluene and centrifugation. The Merrifield resin was dried in vacuo at 40°C for 24h and stored under argon at room temperature.